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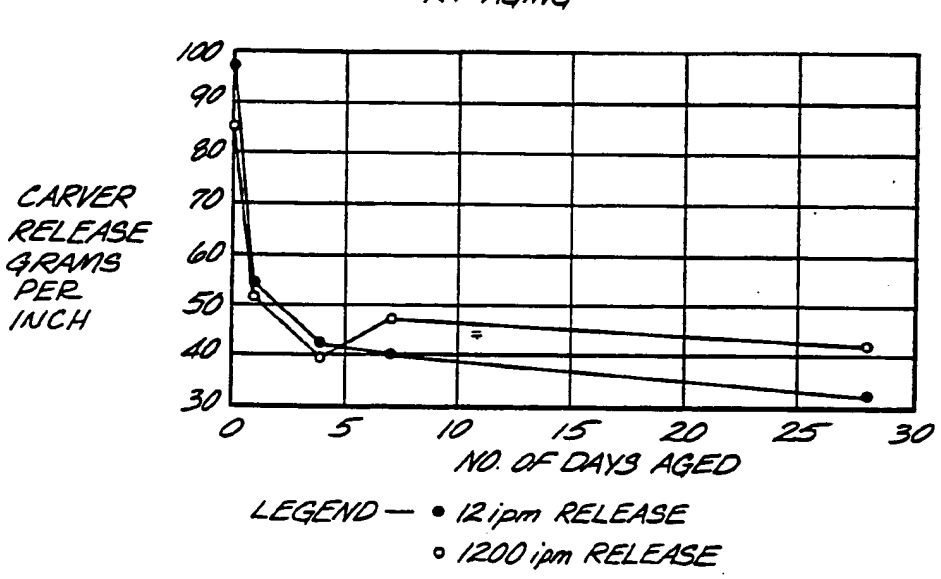

(57) Abstract

Excellent release surfaces are formed by curing a composition which is a dispersion of a reactive silicone present in an amount of from 1 to 30% by weight of the composition as a discontinuous phase in a continuous phase of a reactive resin comprising a reactive oligomer and optionally a reactive monomer. The product has a silicone release surface with silicone anchored in the coating. The surface is for releasable contact with a pressure-sensitive adhesive. Heat, electron beam and/or ultraviolet radiation may be used to achieve cure.

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IMPROVED RELEASE COATINGS

Background of the Invention

The construction of pressure sensitive adhesive products presents a variety of materials selection problems. Basic to any construction is the selection of a suitable release surface.

A label, for instance, is normally comprised of a face stock which may range from paper to a plastic film such as polyester film or even metal; a release liner having a silicone release surface, and a pressure-sensitive adhesive layer, normally rubber or acrylic based in contact with the face stock and the silicone release surface. In self-wound products, a silicone release may be applied to the face stock opposite the side to which the adhesive is applied.

Conventional silicone release coatings are essentially 100% by weight as a silicone resin on a solids basis and by weight the most expensive raw material in label and tape constructions. It would be desirable to reduce the amount of silicone employed as this would reduce the cost of the silicone release surface. Reducing silicone content, however, has a normal effect of increasing the bond to the release surface. As dilution occurs a point is reached where the bond becomes so great that the adhesive may sever the silicone material from the substrate, normally paper, to which it was applied and

in effect transfer the silicone to the adhesive to the detriment of the ability to bond the adhesive to another surface.

U.S. Patent 4,288,479 to Brack is directed to release coatings which contain a waxy material of limited compatibility with a liquid monomer or prepolymer. Upon application to a film, the waxy material migrates to the surface. Radiation is applied to cure the polymer. The waxy material which include silicones are described as generally non-reactive in the polymerizable liquid but can contain reactive groups. In Example 65 of the Brack patent, there is described a release composition containing a silicone rubber which was a polydimethyl siloxane with some unsaturation. On radiation there was stated to be formed a surface releasable with respect to a removable adhesive. We have found that the composition is not functional for permanent pressure sensitives which differ from removable adhesives in that adhesive bond grows with time. As established here, the combination welded together. See Example 5 herein.

The present invention is directed to novel formulations of substantially reduced silicone content which display excellent release properties.

Summary of the Invention

There is provided a substrate having bonded thereto a cured release coating having a silicone release surface for contact with a pressure-sensitive adhesive formed by coreaction of components of a coating composition of a silicone comprised of dimethyl siloxane polymers, preferably a reactive silicone and a resin preferably a reactive resin. The silicone is present in an amount of from about 1 to about 30 percent by weight of the coating composition and anchored to the coating so as to be substantially non-transferable to a pressure-sensitive

adhesive. The silicone release surface is functional to release permanent and removable pressure-sensitive adhesive.

Cure is preferably induced by the action of heat, actinic radiation and/or electron beam radiation, provided in a quantity sufficient to anchor the silicone to the resin whereby the silicone becomes substantially non-transferable to a pressure-sensitive adhesive. Ultraviolet and/or electron beam radiation is presently preferred.

The silicones employed preferably have a molecular weight of at least about 2,000, preferably 10,000 or more.

It is presently preferred that the products be formed by curing a coating comprised of from about 1 to about 30 percent by weight, preferably from about 5 to about 30, most preferably from about 5 to about 15 percent by weight, of a reactive silicone dispersed as a discontinuous phase in a reactive resin present in an amount of from about 99 to about 70 percent by weight, preferably from about 95 to about 70 percent by weight, more preferably from about 95 to about 85 percent by weight, of the combination of the reactive silicone and reactive resin. The reactive resin contains from about 50 to 100 percent by weight reactive oligomer and from about 50 to 0 percent by weight reactive monomer based as the total weight of reactive oligomer and reactive monomer. The reactive monomer is used to control viscosity prior to cure.

To enable good coatability, the dispersion preferably has a viscosity of from about 300 to about 10,000 cps. There may also be included in the system as required photoinitiators, colorants and the like.

The invention enables tailoring of the silicone release surface to the product. Useful products will have TLMI (Tape and Label Manufacturers Institute) peel under Keil conditions of no greater than about 400 N/M. For tapes the TLMI peel should be no greater than about

400 N/M, more typically 100 to 200 N/M. For tags and labels a "high release specification has a TLMI peel up to about 60 to about 100 N/M; a "medium" release has a TLMI peel of about 20 to about 50 N/M; and a "low release" has a TLMI peel of less than about 20. Again all peel values are reported for Keil conditions, namely after aging at a load of 0.25 psi for 20 hours at 70°C.

Brief Description of the Drawings

FIG. 1 illustrates Carver release in grams per inch as a function of aging at room temperature for the composition described in Example 1.

FIG. 2, the Carver release is for the same composition except for aging at 140°F.

FIG. 3 illustrates the release as a function of silicone content of the coating at the time of cure.

FIG. 4 illustrates the same release but after aging for 28 days at room temperature.

FIG. 5 is for the same composition but after aging 28 days at 140°F.

FIG. 6 shows the effect of concentrations of photo initiator on the release force and its effect with time.

Attached drawing marked "Prior Art" depicts the accepted effect on a control release additive on a silicone release material. As can be appreciated by inspection, the release force remains fairly constant until some point is reached where the force increases dramatically. On the scale, zero designates no control release additive while 1 designates no silicone polymer.

Detailed Description

There is provided in accordance with the present invention a substrate having thereon a cured coating of silicone release surface for contact with a pressure-sensitive adhesive. The coating is formed by coreaction of a silicone comprised of dimethyl siloxane polymers, preferably a reactive silicone and a resin, preferably a reactive resin comprising a reactive oligomer. Under curing conditions induced by application of sufficient heat, electron beam (EB) radiation and/or actinic radiation, preferably ultraviolet (UV) radiation, the silicone is anchored to the cured coating and is rendered substantially non-transferable to a pressure-sensitive adhesive in contact with the release surface. The dimethyl siloxane polymer content of the coating is from about 1 to about 30 percent by weight on the total weight of the constituents of the coating with the anchored silicone preferentially concentrated at the surface provided for contact with a pressure-sensitive adhesive. The cured coating may be achieved using silicone-monomer combinations.

Preferential presence of silicone at the surface may be achieved by partial to total incompatibility of the silicone and the resin, or by structural rearrangement of a silicone-resin surface. What is critical is that the silicone is sufficiently anchored to the surface and substantially non-transferable to a pressure-sensitive adhesive. Anchoring may be mechanical and/or chemical.

The desired products have a Carver release as defined herein of less than about 100 grams per inch. Carver release is determined by applying Scotch™ 610 tape to the release surface under a pressure of 6000 psi for 60 seconds then measuring force required to achieve release at a peel rate of 12 inches per minute.

As used herein, by the term "silicone" there is meant dimethyl siloxane polymers consisting of alternate silicone and oxygen atoms with methyl groups attached to silicone. The general structure is:

$$\begin{array}{ccccc} CH_3 & & CH_3 & & CH_3 \\ OSi & O & Si & & OSi \\ CH_3 & & CH_3 & x & CH_3 \end{array}$$

wherein "x" is an integer.

By the term "reactive silicone" there is meant a silicone end capped and/or mid-chain substituted with groups reactive on application of heat and/or energy with reactive groups of the resin. The presently preferred reactive groups are acrylic, mercapto and/or oxirane.

By the term "resin" there is meant an organic moiety which is combinable with the silicone and reactive with silicone and/or reactive silicone under action of heat, actinic radiation and/or electron beam radiation to cause anchoring, preferably preferential surface anchoring of the silicone to the resin.

By the term "reactive resin" there is meant a resin comprising reactive oligomers containing groups which are reactive with the reactive groups of a reactive silicone. The presently preferred reactive oligomers contain reactive acrylic, mercapto and/or oxirane groups. The reactive resin may include a reactive monomer used to control viscosity, although not necessary to utility of the silicones.

By the term "reactive monomer" there is meant monomers which coreact with the reactive silicone and/or the reactive oligomer of the reactive resin and which are effective in reducing viscosity of coating composition used to form the end products of this invention. It is preferred that the reactive monomer be a multifunctional monomer preferably a multifunctional acrylate.

By the term "silicone release surface" there is meant a surface which will release from a pressure sensitive adhesive substantially without transfer of release material to the adhesive and having a TLMI peel under Keil conditions of no greater than about 400 N/M.

It is presently preferred that the products of the invention be formed by coating a substrate such as paper then curing the coating, where the coating is comprised of from about 1 to about 30 percent by weight, preferably about 5 to about 30 percent by weight, more preferably about 5 to about 15 percent by weight, of a reactive silicone dispersed as a discontinuous phase in a reactive resin present in an amount of from about 99 to about 70 percent by weight, preferably from about 95 to about 70 percent by weight, more preferably from about 95 to about 85 percent by weight of the combination of the reactive silicone and reactive resin. The reactive resin contains from about 50 to 100 percent by weight reactive oligomer and from about 50 to 0 percent by weight reactive monomer based as the total weight of reactive oligomer and reactive monomer. The reactive monomer is used to control viscosity prior to cure. There may also be included in the system as required photoinitiators, colorants and the like.

To enable good coatability, the dispersion should have a viscosity of from 300 to about 10,000 cps. Viscosity can, as indicated, be adjusted by the addition of reactive monomers.

While not bound by theory, it is presently believed that surface reorientation occurs to form the silicone release surface. Reorientation can occur either prior to, during or following cure, as it has been observed, the quality of release of the silicone release surface can increase with time, even a fairly short time span, and then level out. Improved release is attributed to the

amount of silicone at the surface. The cured coating is believed similar to block or graft copolymers having oligomer blocks bound to the silicone blocks with preferential presence of silicone at the surface as opposed to the body of the coating. The coating typically has a glass transition temperature of at least 0°C, preferably greater than about 20°C.

Critical to the use of a dispersion is that the proportion of reactive silicone and reactive resin remain as a coatable dispersion in which the reactive silicone is as the dispersed phase and the reactive resin is the continuous phase. Once a certain level of reactive silicone monomer content is reached, phase inversion begins, to the end of forming a system in which the reactive resin is the dispersed phase and the reactive silicone is the continuous phase. When this is complete, the cured product will become rubbery and behave like a conventional silicone release coating which requires a high concentration of silicone before a suitable release level is achieved.

In the practice of the invention, the dispersion is coated in a conventional manner onto a substrate which may be any grade of paper, including the papers of low grade, cardboard, polymeric films and the like. Cure is to be sufficiently complete, such that substantially no silicone transfers to a pressure-sensitive adhesive to which the silicone release surface contacts. Avoidance of transfer is the result of the silicone being anchored to coating body and not available to transfer to the pressure-sensitive adhesive.

Electron beam cure has a particular benefit, since it can initiate reaction of resins with substantially non-reactive silicones to produce a functional release surface. The ability of the coating to accept colorants

is a desirable feature for establishing the presence and uniformity of the release coating.

What is produced by the practice of the invention is a unique product of low silicone content but having a silicone release surface having excellent release properties. The coating is hard and substantially non-stretchable and aggressively bound to the substrate to which it is applied. Substantially complete cure insures against transfer to the adhesive during the lifetime of a laminate or self-wound product. The release coatings of this invention provides the advantage that the release force can be relatively constant over broad range of stripping speeds without the silicone substantially transferring to the adhesive surface. High holdout can be achieved on low grade papers and monomers can be used not only to adjust viscosity but also adjust release force.

In the following Examples TLMI Release is by Test Method VII LD-468 and PSTC Test No. 2. Loop Tack is by PSTC - Test No. 5. Keil release values are after aging under a force of 0.25 psi for 20 hours at 70°C. TLMI means Tape and Label Manufacturers Institute and PSTC means Pressure Sensitive Tape Council. Except for the removable adhesive identified as part of Example 1, the adhesives employed in the Examples were permanent rubber based and/or acrylic based pressure-sensitive adhesives.

EXAMPLE 1 (FIGS. 1-6)

A master batch of a resin coating designated as AE-508 was formed of 72 parts by weight acrylated epoxy oligomer (Celanese 3703) supplied by Celanese Corp., 16 parts by weight hexanedioldiacrylate (HDODA) and 12 parts by weight diethoxyacetophenone (DEAP). From 80-95 parts of the master batch was mixed with 20-5 parts Dehesive™ VP-1530, a mixture acrylated and thiol and functional polysiloxanes, available from Stauffer-Wacker

Silicones Co. (S-1530 herein). The mixtures were prepared in select increments of weight percent silicone.

The coating mixtures were applied on clay coated gloss paper.

The coated paper was exposed to the UV radiation given off by two medium pressure mercury vapor lamps at 200 watts/inch at web speed of 50 feet per minute. This corresponds to an energy input of about 5 kilojoules per square meter. Exposure resulted in cure to a hard glossy film which was dry to the touch. Completeness of cure was determined by laminating Scotch™ 610 tape manufactured by 3M, under pressure and measuring the force required to delaminate the construction or remove the tape. Release which is stable and low over time without substantially detackifying the adhesive is one indication of complete cure.

Cured coatings with varying amounts of S-1530 were tested using the Carver release test which consists of laminating the cured release liner to Scotch™ 610 tape under a pressure of 6,000 psi for 60 seconds, and measuring force required to achieve release at a peel rate of 12 inches per minute (ipm). Release measurements were modified to include a 1200 inches per minute (ipm) rate. The release test as applied to aged samples was after aging with the test tape applied just before measuring release values.

The initial formulation consisted of 90% AE 508 and 10% S-1530. As shown in FIGS. 1 and 2, the initial Carver Release values were between 80-100 grams. Aging at room temperature or 140°F, resulted in a rapid decline to a stable release level within the range of 20-50 grams.

FIGS. 3, 4 and 5 show the results of varying the concentration of S-1530 on Initial Peel (FIG. 3) after room temperature (RT) aging (FIG. 4) and elevated temperature aging (FIG. 5). The results display a phenomenon

that appears to be related to phase transition. As silicone content increases there is reached a point where a transition to a rubbery phase occurs. The system then behaves in a conventional way, with release force decreasing with an increase in silicone content.

More particularly, FIG. 3 shows the initial Carver Release results and shows low initial releases (both 12 and 1200 ipm) in the range of 3%-5% S-1530. In the range of 10%-40% S-1530 initial release values increase, with 1200 ipm releases actually appearing to be lower than 12 ipm. By 40%, S-1530 12 ipm release values decline while 1200 ipm releases increase rapidly and appear to level off above 50% S-1530.

FIGS. 4 and 5 show the Carver release values for samples aged 28 days at RT and 140°F. Formulations in the 5%-20% S-1530 range yield release values in the range of 20-40 grams with minimal differences between 12 and 1200 ipm releases. Above about 30% S-1530, the release values climb rapidly, peak, and then decline as the percentage of S-1530 increases beyond 40%. The range beyond 60% S-1530 is again characterized by a marked difference between 12 and 1200 ipm release values. The region up to 20 percent is hard and glassy with desirable release values. Above about 30% S-1530 a phase inversion occurs to a rubbery phase which is characteristic of conventional release liners.

The concentration of photoinitiator diethyl acetophenone (DEAP) in the formulation has a significant effect on the initial Carver release values of lab samples. As shown in FIG. 6, the formulation with an excessive amount of DEAP (20%) yields initially high Carver release values, which subsequently age down to a level similar to formulations with 1%-5% DEAP. This is similar to the aging down observed in FIGS. 1 and 2 are for formulations having a concentration of 10.8% DEAP.

Constructions using a rubber based hot melt removable adhesive and a high tack, high peel rubber based hot melt adhesive, were made and found to have acceptable low release from the surface to 10% S-1530. Constructions using 4, 6 and 10% S-1530 were prepared using a removable adhesive. Formulations using 6 and 10% S-1530 had low release whereas the formulation using 4% silicone had tighter release as measured by subjective testing.

EXAMPLE 2

There was evaluated the performance of AE-508 with various reactive silicones as against their performance as homopolymers. The control was a standard thermally cured silicone release liner. The reactive silicones were S-450, an end acrylated silicone known as RC-450 supplied by Goldsmith Chemical Corporation; S-1559, a mixture of acrylated and mercapto functional silicone known as Dehesive^{TM} VP-1559 supplied by Stauffer Wacker-Silicone Corp.; S-4818, an end and in chain acrylated silicone known as IC-4818-38 supplied by Lord Chemical Company and S-5360 and S-6350, each end and in chain acrylated silicones known respectively as Ebecryl 19-6360 and 19-6350, supplied by U.C.B. Radcure Inc.

Table 1 shows performance with an acrylic adhesive while Table 2 shows performance with a rubber based adhesive. In the Table, homopolymer means 100% of the reactive silicone; copolymer means 80% by weight AE-508 and 20% by weight reactive silicone. In each instance the coating was formed on a super calendered kraft paper and EB cured at a dosage of 30 kGy.

The conclusion drawn was that the copolymers served as useful release agents as did the most costly homopolymers.

TABLE 1

Homopolymer	TLM1 Peel 300 ipm(N/M) 3 Day	Keil	Loop Tack (N/M) 3 Day
S-450	69	54	450
S-1559	22	44	340
S-4818	18	40	405
S-6360	134[1]	138[1]	335
S-6350	119	168	130
Copolymer			
S-450	64[1]	36[2]	165
S-1559	36	28[2]	455
S-4818	30[1,2]	37[2]	445
S-6360	60[1,2]	46[1,2]	515
S-6350	87[1,2]	111[2]	515
Control	6	6	400

1 Release Pickoff at Slow Speeds
2 Zippy Release

TABLE 2

Homopolymer	TLM1 Peel 300 ipm(N/M) 3 Day	Keil	Loop Tack (N/M) 3 Day	Keil
S-450	4	7	1895	1980
S-1559	5	8	1615	1655
S-4818	3	5	1575	1715
S-6360	5	22[2]	1720	1850
S-6350	8	12[2]	1065	1280
Copolymer				
S-450	7	10	1870	1835
S-1559	6	5	1790	1655
S-4818	4	4	1770	1495
S-6360	26[2]	39[1]	1990	1750
S-6350	14[2]	20[2]	1950	1695
Control	4	6	1625	1590

1 Release Pickoff at Slow Speeds
2 Zippy Release

EXAMPLE 3

The following is to show the effect of using the different oligomer and monomer combinations to enable control of release. With reference to Table 2, resins 19-6810, 19-6830 and 19-6657 are acrylated polyesters sold by U.C.B. Radcure, Inc.; PES-166 and PES-169 are acrylated urethanes sold by Polymer Systems Corporation; "BPA diacryl" is an acrylated bisphenol-A epoxy resin; C-9003 is an aliphatic triacrylate. The control was a commercial release liner having a 100% silicone surface. The adhesive employed was a tackified Kraton-1107, a styrene-isoprene, styrene-isoprene-styrene resin rubber manufactured and sold by Shell Chemical Company. The formulation in each instance was 70% by weight resin or monomers, 20% by weight hexanedioldiacrylate (HDODA) and 10% by weight S-1559. Cure was by electron beam at a dosage of 30 kGy in the presence of 200-250 ppm oxygen. Results shown in Table 3 established that epoxy, urethane and polyester oligomers gave low release values whereas an aliphatic oligomer gave higher release.

TABLE 3

Resin	Description	TIMI RELEASE (N/M)		LOOP TACK (N/M)	
		One Day	Keil	One Day	Keil
19-6810	Polyester	7	14	590	630
19-6830	Polyester	34	26	980	690
19-6657	Polyester	19	22	690	710
PES-166	Urethane	1	10	690	710
PES-169	Urethane	8	11	670	650
SR-349	BPA Diacryl	1	19	690	590
C-9003	Aliphatic Triac	75	88	590	530
Control		—	—	850	650

EXAMPLE 4

In Example 65 of U.S. Patent 4,228,479 to Brack, there is disclosed a potential formulation for a release surface. The formulation was prepared with certain substitutions made because of the lack of availability of components. The substitutions were not believed to modify the performance as the controlling ingredient was the silicone employed. The base formulations are shown in Table 4.

TABLE 4

COMPONENTS

EXAMPLE 65	FORMULATION A
66 Parts Trifunctional Urethane	PES-166 Difunctional Urethane
68 Parts 1,4-Butane Diol Diacrylate	1,6 Hexane Diol Diacrylate
50 Parts Acrylated Epoxidized Soya Oil	same
72 Parts Trimethylolprop. Tri Acry	same
1.5 Parts 2-Hydroxy Ethyl Acrylate	1,4-Butane Diol Monoacrylate
2 Parts Stearyl Acrylate	same
5 Parts W-982 Silicone Gum (0.2% vinyl)	Several Variations
16 Parts Benzoin Isobutyl Ether	Benzoin Isopropyl Ether

Since Brack taught the use of a silicone of low functionality there was employed as a representative of the silicone contemplated by the patentee, 0.2% VOC, which was a 0.2% vinyl end capped polydimethyl siloxane. Their performance with respect to a hot melt rubber base adhesive and an acrylic adhesive are formulations A to B of Tables 5 and 6. UV cured formulations as suggested by Brack were regarded as nonfunctional as a release surface as the Keil values for the loop tack could not even be measured due to welding. It was surprisingly found that high energy dosage available by electron beam cure could produce functional release materials. When formulation A was used with the silicones of the instant invention, namely formulations C and D, they as well as formulations E to H at all times a functional release surface formed under both UV and EB conditions. In the process,

a master batch of all components except the silicone formulation was prepared. The various formulations were prepared by taking a portion of the master batch and adding the silicone and photo-initiators as required. Samples were coated on super-calendared kraft paper and cured by either UV or EB radiation. The cured samples were then laminated to freshly prepared dry adhesives on polyester films. They were aged for one day under Keil conditions (70°C, 0.25 psi for 20 hours) and TLMI release measured at 300 inches per minute; the results including loop tack data measured are reported in Tables 5 (rubber based permanent adhesive) and 6 (acrylic based permanent adhesive).

TABLE 5

Form	Resin	Silicone	SI%	Cure	TLMI Release(N/M)		Loop Tack(N/M)	
					One Day	Keil	One Day	Keil
A	A	0.2% VEC+BIPE	1.8	UV	40	WELD	1340	—
B	A	0.2% VEC+BIPE	10	UV	35	WELD	700	—
C	A	S-1559	1.8	EB	7	32	1880	1830
D	A	S-1559	10	EB	7	24	1450	1720
E	AE-508	S-1559+BIPE	10	UV	2	1	1000	900
F	AE-508	S-1559+12BIPE	10	UV	2	1	1240	920
G	AE-508	S-1559+12DEAP	10	UV	35	5	1140	1150
H	AE-508	S-1559	10	EB	6	12	1635	1700
Control			100	—	3	8	1700	1750

Form = Formulation

TABLE 6

Form	Resin	Silicone	SI%	Cure	TIMI Release(N/M) One Day	TIMI Release(N/M) Keil	Loop Tack(N/M) One Day	Loop Tack(N/M) Keil
A	A	0.2% VEC+BIPE	1.8	UV	140	WELD	—	—
B	A	0.2% VEC+BIPE	10	UV	160	WELD	—	—
C	A	S-1559	1.8	EB	110	93	420	520
D	A	S-1559	10	EB	100	30	370	340
E	AE-508	S-1559+BIPE	10	UV	30	55	300	220
F	AE-508	S-1559+12BIPE	10	UV	25	50	—	300
G	AE-508	S-1559+12DEAP	10	UV	55	67	—	160
H	AE-508	S-1559	10	EB	70	100	420	550
Control			100	—	100	150	400	220

Cure Dose: EB=30KGy;UV=2x200Watts/Inch Lamps, 50 ft/min.
VP-1559 Radiation Curable Silicone Coating from SWS Silicones
0.2% VEC = 0.2% Vinyl Encapped Polydimethylsiloxane
BIPE=6% Benzoin Isopropyl Ether, 12BIPE=12% Benzoin Isopropyl Ether
12DEAP=12% Diethoxyacetophenone
Form = Formulation

EXAMPLE 5

Formulation AE-508 was as a base formulation employing GE 479-1866 an experimental epoxy functional silicone provided by General Electric Company, Silicone Products Division. The formulations are shown in Table 7 and Carver release results reported after UV cure using 2 lamps at 200 watts per inch at a web speed of 50 feet per minute are shown in Table 8. Results are high average or highest value.

TABLE 7

Formulation, Percent By Weight	A	B	C
AE-508	95	94	89
GE 479-1866	5	5	10
Additional Photoinitiator	0	1	1

TABLE 8

Carver Peel in grams/inch at	Formulation A	B	C
I. 12 ipm at			
R.T., initial	55	7	(a)
7 days	13	10	3
14 days	11	-	-
28 days	7	4	3
140°F - 7 days	13	12	8
14 days	24	20	4
28 days	13	7	4
II. 1200 ipm at			
R.T., initial	195	65	62
7 days	48	54	68
14 days	54	60	77
28 days	54	61	64
140°F - 7 days	45	48	53
14 days	57	60	71
28 days	48	52	42

(a) Too low to measure

EXAMPLE 6

Tests were conducted to show the effect of using the different oligomers and silicone combinations to enable control of release. With reference to Table 9, resin Valspar™ S-9783-002 a mixture of acrylated oligomers provided by Valspar Co. was mixed with S-450 in varying amounts coated and EB cured (30kGy) on a polypropylene release backing. Peel was measured with respect to a permanent rubber based pressure sensitive adhesive.

TABLE 9

% S-450	% OLIGOMER	KEIL RELEASE (N/M)	180° PEEL (N/M)
5	95	300	460
10	90	170	440
15	85	120	440

EXAMPLE 7

The data of Table 10 shows the effect of using the different monomer combinations on release. The monomers were pentaarythritoltriacrylate (PETA), hexanediol-diacrylate (HDODA) and 2-ethylhexyl acrylate (2EHA).

TABLE 10

% S-450	% 2-EHA	% PETA	% HDODA	KEEL RELEASE (N/M)	LOOP TACK (N/M)
25	-	-	75	80	600
25	25	25	25	9	650
25	-	25	50	170	400

EXAMPLE 8

A mixture of 20 parts trimethylopropanetriacrylate, 40 parts Celrad 3201, an acrylated polyester from Celanese, Inc., 10 parts N-vinylpyrrolidone and 1.5 parts S-6350 and 2 parts photo initiator was coated onto crepe paper and cured with enough actinic (UV) radiation to give a hard dry film. The release liner was Keil aged against a permanent rubber based pressure sensitive adhesive. The Keil release forces were 80-150 N/M with minimal loss of adhesive tack.

WHAT IS CLAIMED IS:

1. A product comprising a substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive said coating formed by coreaction of a silicone comprised of dimethyl siloxane polymers and a resin contained in a coating composition applied to the substrate, the silicone being present in an amount of from about 1 to about 30 percent by weight of the coating and sufficiently anchored to the coating to be substantially non-transferable to a pressure-sensitive adhesive.

2. A product as claimed in claim 1 in which the silicone is present in an amount of from 5 to about 15 percent by weight of the coating.

3. A product comprising substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive said coating formed by coreaction of silicone present in an amount of from about 1 to about 30 percent by weight of the coating and a resin contained in a coating composition applied to the substrate, the cure induced by exposure of the applied coating to the action of energy supplied by heat, actinic radiation, electron beam radiation, or combinations thereof induced in a sufficient amount to anchor the silicone to the coating whereby the silicone is substantially non-transferable to a pressure-sensitive adhesive.

4. A product as claimed in claim 3 in which the silicone is present in an amount of from about 5 to about 15 percent by weight of the coating.

5. A product comprising a substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and said coating formed by coreaction of a reactive silicone present in an amount of from about 1 to about 30 percent by weight of the coating and a reactive resin comprised of reactive oligomers contained in a coating composition applied to the substrate, the cure induced by the action of energy supplied by heat, actinic radiation, electron beam radiation, or a combination thereof and induced in an amount sufficient to anchor the silicone to the coating whereby the silicone is substantially non-transferable to a pressure-sensitive adhesive.

6. A product as claimed in claim 5 in which the silicone is present in an amount of from about 5 to about 15 percent by weight of the coating.

7. A product comprising a substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and said coating formed by coreaction of a reactive silicone present in an amount of from about 1 to about 30 percent by weight of the coating and a resin comprised of reactive oligomers, said reactive silicone being at least partially immiscible in said coating composition, the cure induced by the action of energy supplied by heat, actinic radiation, electron beam radiation, or a combination thereof induced to the coated substrate in sufficient amount to anchor the silicone to the coating whereby the silicone is substantially non-transferable to a pressure-sensitive adhesive.

8. A product as claimed in claim 7 in which the silicone is present in an amount of from about 5 to about 15 percent by weight of the coating.

9. A product as claimed in claim 1 which includes a colorant.

10. A product as claimed in claim 7 which includes a colorant.

11. A product comprising a substrate having coating on at least one side thereof with a cured coating composition comprised of from about 1 to about 30 percent by weight of the coating composition of a reactive silicone dispersed as a discontinuous phase in about 99 to about 70 percent by weight of the coating composition or continuous reactive resin phase comprising from about 50 to 100 percent by weight of the oligomer reactive with said reactive silicone and from about 50 to 0 percent by weight of the reactive resin of a reactive monomer, said reactive silicone being a polydimethyl siloxane having a molecular weight of at least about 2000 and having pendent therefrom sufficient reactive groups to react with the reactive groups of the oligomer, said coating being cured on exposure to the action of electron beam radiation, ultraviolet radiation, heat or a combination thereof to form cured coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive with substantially all of the silicone contained in the coating composition being anchored to the cured coating and substantially non-transferable to a pressure-sensitive adhesive.

12. A product as claimed in claim 11 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

13. A product as claimed in claim 11 in which the oligomers are selected from the group consisting of acrylated epoxies, acrylated polyesters, acrylated polyurethanes and mixtures thereof.

14. A product as claimed in claim 11 in which the reactive monomer is a multifunctional monomer.

15. A product as claimed in claim 12 in which the reactive monomer is a multifunctional monomer.

16. A product as claimed in claim 15 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

17. A product as claimed in claim 11 in which the reactive groups of the silicone are selected from the group consisting of acrylic groups and mercaptos groups, oxiranes and mixtures thereof.

18. A product as claimed in claim 12 in which the reactive groups of the silicone are selected from the group consisting of acrylic groups, mercapto groups, oxiranes and mixtures thereof.

19. A product as claimed in claim 16 in which the reactive groups of the silicone are selected from the group consisting of acrylic groups, mercapto groups, oxiranes and mixtures thereof.

20. A curable coating composition comprising from about 1 to about 30 percent by weight of the coating composition of a reactive silicone dispersed as a discontinuous phase in 99 to 70 percent by weight of the coating composition of reactive resin phase comprising:

(i) from 50 to 100 percent by weight of the reactive resin of an oligomer reactive with said reactive silicone and

(ii) from about 50 to 0 percent by weight of the reactive resin of a reactive monomer, said reactive silicone being a polydimethyl siloxane having a molecular weight of at least about 2000 and having pendent therefrom sufficient reactive groups to react with the reactive group of the oligomer on exposure to the action of electron beam radiation, ultraviolet radiation or heat to form a cured coating having a silicone release surface releasable from a pressure-sensitive adhesive and in which substantially all of the silicone contained in the composition is anchored to the coating to substantially prevent transfer of the coating to a pressure-sensitive adhesive.

21. A curable composition as claimed in claim 20 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

22. A curable coating as claimed in claim 20 in which the oligomers are selected from the group consisting of acrylated epoxies, acrylated polyesters, acrylated polyurethanes and mixtures thereof.

23. A curable coating as claimed in claim 20 in which the reactive monomer is a multifunctional monomer.

24. A curable coating as claimed in claim 22 in which the reactive monomer is a multifunctional monomer.

25. A curable composition as claimed in claim 24 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

26. A curable coating as claimed in claim 20 in which the reactive groups of the silicone are selected from the groups consisting of acrylic groups, mercapto groups, oxirane groups and mixtures thereof.

27. A curable coating as claimed in claim 21 in which the reactive groups of the silicone are selected from the groups consisting of acrylic groups, mercapto groups, oxirane groups and mixtures thereof.

28. A curable coating as claimed in claim 25 in which the reactive groups of the silicone are selected from the groups consisting of acrylic groups, mercapto groups, oxirane groups and mixtures thereof.

29. A curable coating composition comprising:

(a) from about 5 to about 15 percent by weight of the coating composition of a reactive silicone having reactive groups selected from acrylic groups, mercapto groups, oxirane groups and mixtures thereof, dispersed as discontinuous phase in a from 95 to about 85 percent by weight of the coating composition of a continuous reactive resin phase comprising:

(i) from about 50 to 100 percent by weight of the reactive resin of an oligomer reactive with said reactive silicone and selected from the group consisting

of acrylated epoxy resins, acrylated polyester resins, acrylated urethane resins and mixtures thereof, and

(ii) from 50 to about 0 percent by weight of the reactive resin of at least one acrylated multifunctional monomer, said reactive silicone being a polydimethylsiloxane having a molecular weight of at least about 2,000, said composition having a viscosity of from about 300 to about 10,000 centipoise and curable on exposure to the action of electron beam radiation, ultraviolet radiation or heat, or a combination thereof, to form a cured coating having a silicone release surface opposed the substrate to which the coating has been applied for releasable contact with a pressure-sensitive adhesive and in which substantially all of the silicone contained in the composition is anchored in the coating and substantially nontransferable to a pressure-sensitive adhesive.

30. A process for producing a release coated substrate which comprises:

(a) applying to a substrate a coating composition comprising:

(i) from about 1 to about 30 percent by weight of the composition of a reactive silicone dispersed as a discontinuous phase in from about 99 to about 70 percent by weight of the coating composition of a continuous reactive resin phase comprising:

(ii) from about 50 to 100 percent by weight of reactive resin phase of an oligomer reactive with said reactive silicone, and

(iii) from about 50 to 0 percent by weight of the reactive resin phase of a reactive monomer, said reactive silicone being a polydimethylsiloxane having a molecular weight of

at least about 2,000 and having pendent therefrom sufficient reactive groups to react with the reactive groups of the oligomer;

(b) exposing the coating to the action of sufficient electron beam radiation, ultraviolet radiation or heat or a combination thereof to form a cured coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and in which substantially all of the silicone groups are anchored in the cured coating and substantially non-transferable to a pressure-sensitive adhesive.

31. A process as claimed in claim 30 in which coating composition has a viscosity of from about 300 to about 10,000 centipoise.

32. A process as claimed in claim 30 in which the oligomers are selected from the group consisting of acrylated epoxies, acrylated polyesters, and acrylated polyurethanes and mixtures thereof.

33. A process as claimed in claim 30 in which the reactive monomer is a multifunctional monomer.

34. A process as claimed in claim 32 in which the reactive monomer is a multifunctional monomer.

35. A process coating as claim in claim 30 in which the reactive groups of the silicone are selected from the groups consisting of acrylic groups, mercapto groups, oxirane groups and mixtures thereof.

36. A curable coating as claimed in claim 32 in which the reactive groups of the silicone are selected

from the groups consisting of acrylic groups, mercapto groups, oxirane groups and mixtures thereof.

37. A curable coating as claimed in claim 34 in which the reactive groups of the silicone are selected from the group consisting of acrylic groups and mercapto groups and mixtures thereof.

38. A process for forming a release coating substrate which comprises:

(a) applying to the substrate a coating comprising:

(i) from about 5 to about 15 percent by weight of the coating of a reactive silicone having reactive groups selected from acrylic groups, mercapto groups, oxirane groups and mixtures thereof, dispersed as discontinuous phase in from about 95 to about 85 percent by weight of the coating of a continuous reactive resin phase comprising:

(ii) from 50 to 100 percent by weight of the reactive resin of an oligomer reactive with said reactive silicone and selected from the group consisting of acrylated epoxy resins, acrylated polyester resins, acrylated urethane resins and mixtures thereof, and

(iii) from about 50 to 0 percent by weight of the reactive resin of at least one multifunctional monomer, said reactive silicone being a polydimethyl-siloxane having a molecular weight of at least about 2,000, said coating composition having a viscosity of from about 300 to about 10,000 centipoise;

(b) subjecting the coating to the action of sufficient electron beam radiation, ultraviolet radiation

or heat or a combination thereof to form a cured coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and in which substantially all of silicone is anchored in the cured coating and substantially non-transferable to a pressure-sensitive adhesive.

39. A product comprising substrate having bonded thereto a cured release coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive, said coating formed by coreaction of silicone present in an amount of from about 1 to about 30 percent by weight of the coating and a resin contained in a coating composition applied to the substrate, the cure induced by exposure of the applied coating to the action of energy supplied by ultraviolet radiation, electron beam radiation, or a combination thereof induced in a sufficient amount to anchor the silicone to the coating whereby the silicone is substantially non-transferable to a pressure-sensitive adhesive.

40. A product as claimed in claim 39 in which the silicone is present in an amount of from about 5 to about 30 percent by weight of the coating.

41. A product as claimed in claim 39 in which the silicone is present in an amount of from 5 to about 15 percent by weight of the coating.

42. A product comprising a substrate having coating on at least one side thereof with a cured coating composition comprised of from about 1 to about 30 percent by weight of the coating composition of a reactive silicone dispersed as a discontinuous phase in about 99 to about 70 percent by weight of the coating composition or con-

tinuous reactive resin phase comprising from about 50 to 100 percent by weight of the oligomer reactive with said reactive silicone and from about 50 to 0 percent by weight of the reactive resin of a reactive monomer, said reactive silicone being a polydimethyl siloxane having a molecular weight of at least about 2000 and having pendent therefrom sufficient reactive groups to react with the reactive groups of the oligomer, said coating being cured on exposure to the action of electron beam radiation, ultraviolet radiation, or a combination thereof to form cured coating having a silicone release surface releasable from a pressure-sensitive adhesive with substantially all of the silicone contained in the coating composition being anchored to the cured coating.

43. A product as claimed in claim 42 in which the reactive silicone is present in an amount of from about 5 to about 30 percent by weight of the coating composition.

44. A product as claimed in claim 42 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

45. A curable coating composition comprising from about 1 to about 30 percent by weight of the coating composition of a reactive silicone dispersed as a discontinuous phase in 99 to 70 percent by weight of the coating composition of reactive resin phase comprising:

(i) from 50 to 100 percent by weight of the reactive resin of an oligomer reactive with said reactive silicone and

(ii) from about 50 to 0 percent by weight of the reactive resin of a reactive monomer, said reactive silicone being a polydimethyl siloxane having a molecular

weight of at least about 2000 and having pendent therefrom sufficient reactive groups to react with the reactive group of the oligomer on exposure to the action of electron beam radiation, ultraviolet radiation or a combination thereof to form a cured coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and in which substantially all of the silicone contained in the composition is anchored to the coating to prevent transfer to a pressure-sensitive adhesive.

46. A curable composition as claimed in claim 45 in which the reactive silicone is present in an amount of from about 5 to about 30 percent by weight of the coating composition.

47. A curable composition as claimed in claim 45 in which the reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the coating composition.

48. A process for producing a release coated substrate which comprises:

(a) applying to a substrate a coating composition comprising:

(i) from about 1 to about 30 percent by weight of the composition of a reactive silicone dispersed as a discontinuous phase in from about 99 to about 70 percent by weight of the coating composition of a continuous reactive resin phase comprising:

(ii) from about 50 to 100 percent by weight of reactive resin phase of an oligomer reactive with said reactive silicone, and

(iii) from about 50 to 0 percent by weight of the reactive resin phase of a reactive

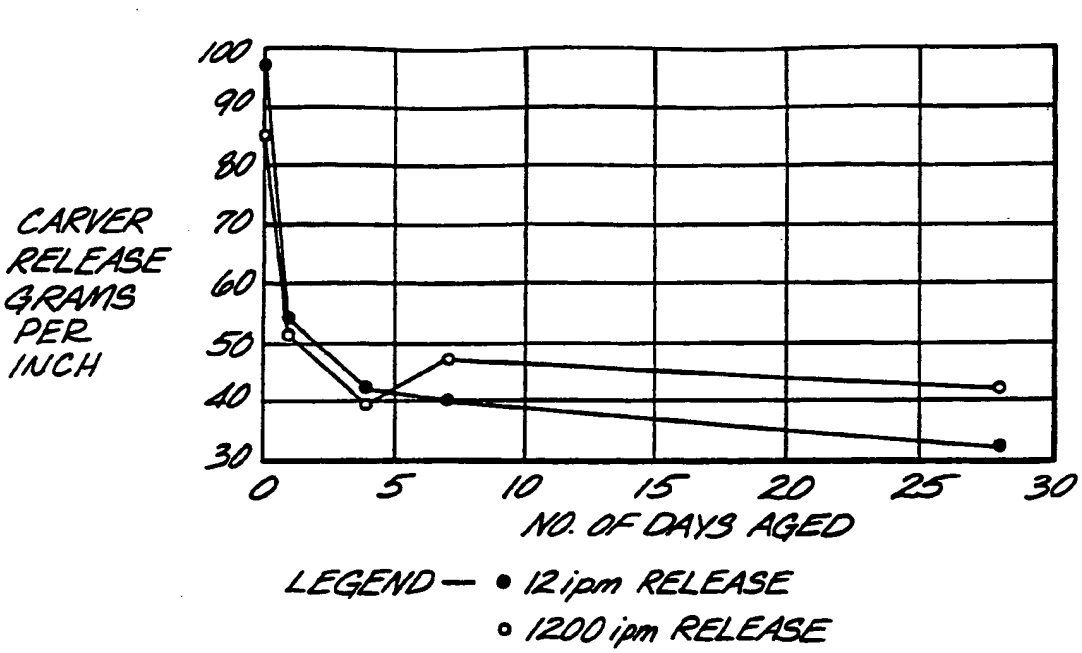
monomer, said reactive silicone being a polydimethylsiloxane having a molecular weight of at least about 2,000 and having pendent therefrom sufficient reactive groups to react with the reactive groups of the oligomer;

(b) exposing the coating to the action of sufficient electron beam radiation, ultraviolet radiation or a combination thereof to form a cured coating having a silicone release surface for releasable contact with a pressure-sensitive adhesive and in which substantially all of the silicone groups are anchored in the cured coating and substantially non-transferable to a pressure-sensitive adhesive.

49. A process as claimed in claim 48 in which reactive silicone is present in an amount of from about 5 to about 30 percent by weight of the composition.

50. A process as claimed in claim 48 in which reactive silicone is present in an amount of from about 5 to about 15 percent by weight of the composition.

Fig. 1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CARVER RELEASE GRAMS PER INCH
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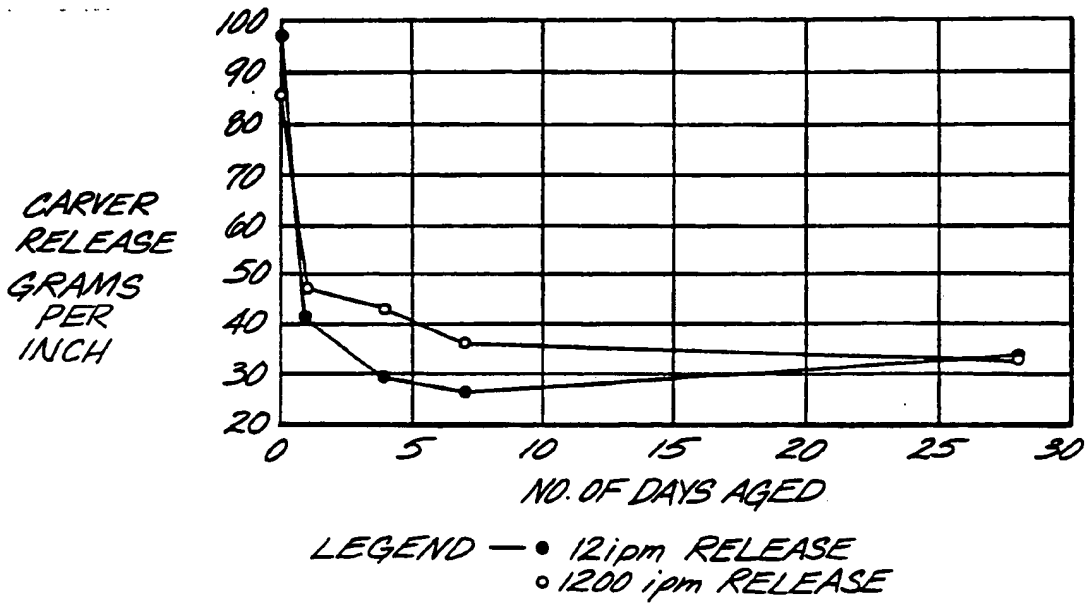
∘ 1200 ipm RELEASE

Fig. 2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50
40
30
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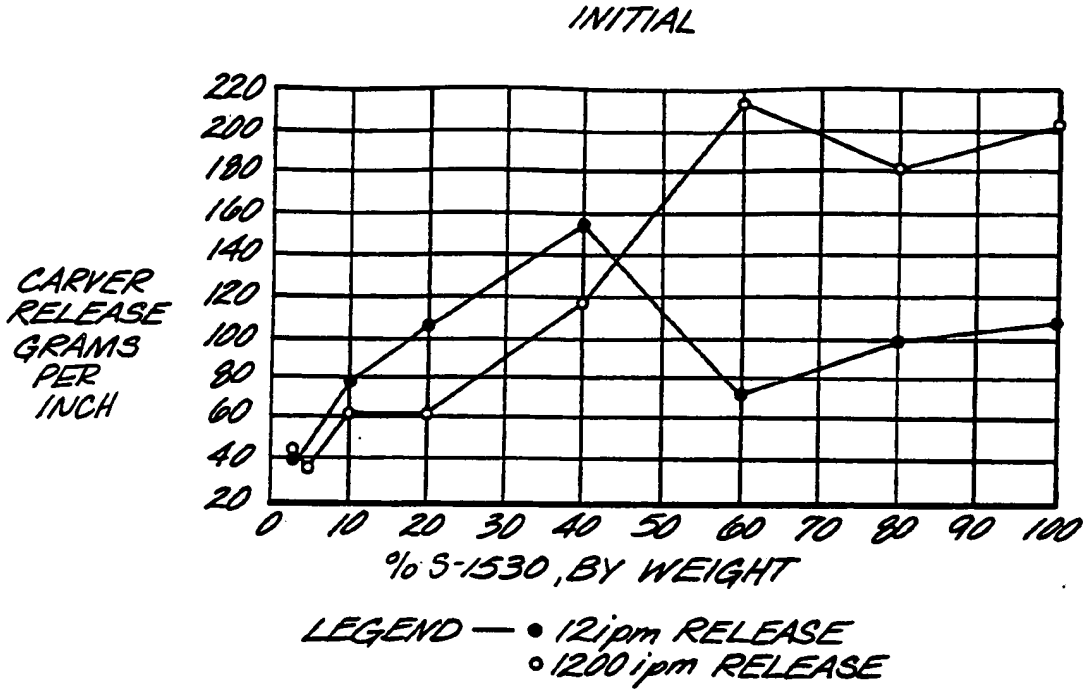
15
20
25
30
NO. OF DAYS AGED
LEGEND — • 12 ipm RELEASE
∘ 1200 ipm RELEASE

Fig. 3


INITIAL
CARVER RELEASE GRAMS PER INCH
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200
180
160
140
120
100
80
60
40
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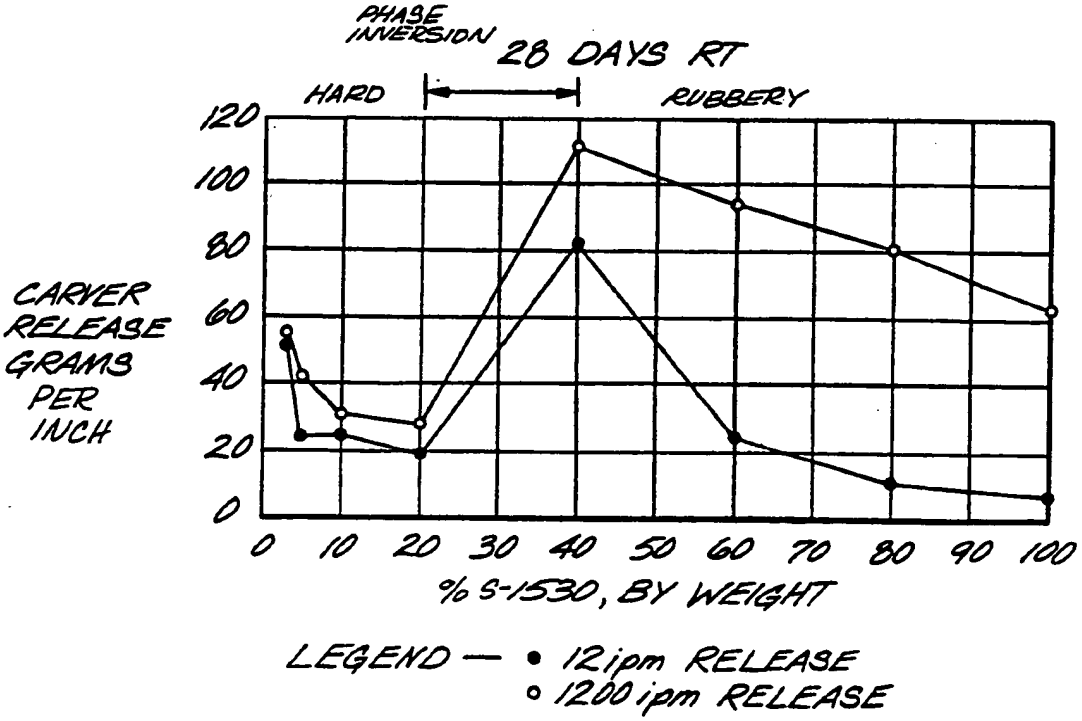
0 10 20 30 40 50 60 70 80 90 100
% S-1530, BY WEIGHT
LEGEND — • 12 ipm RELEASE
∘ 1200 ipm RELEASE

Fig. 4


PHASE INVERSION
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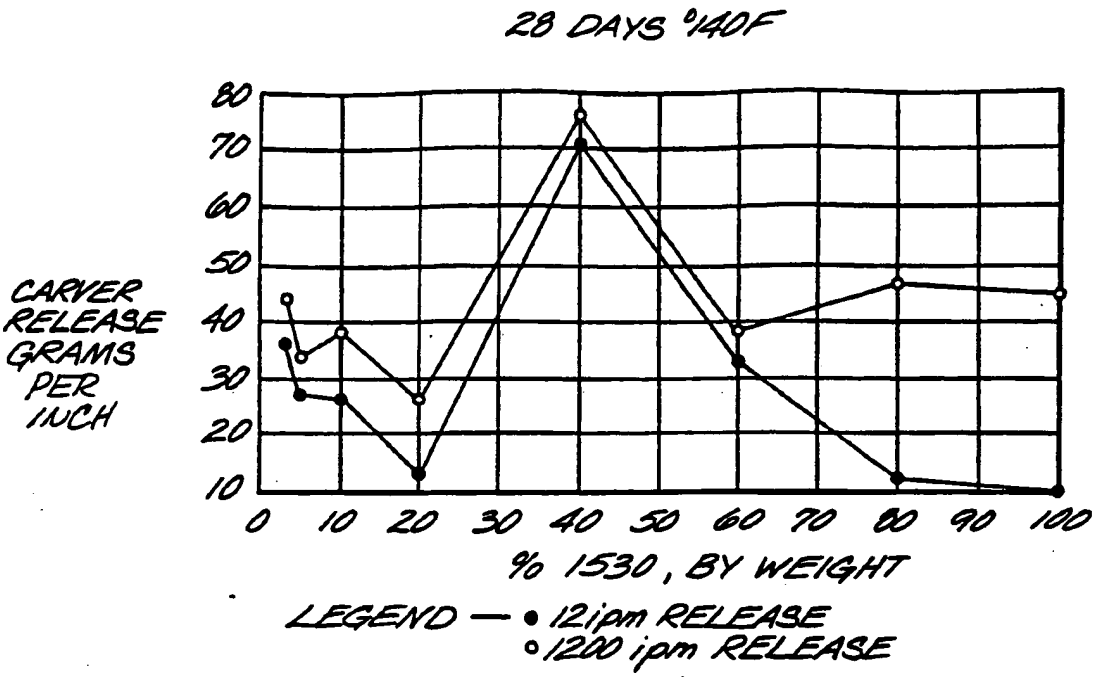
HARD
RUBBERY
CARVER RELEASE GRAMS PER INCH
120
100
80
60
40
20
0
0 10 20 30 40 50 60 70 80 90 100
% S-1530, BY WEIGHT
LEGEND — • 12 ipm RELEASE
∘ 1200 ipm RELEASE

Fig. 5


28 DAYS °140F
CARVER RELEASE GRAMS PER INCH
80
70
60
50
40
30
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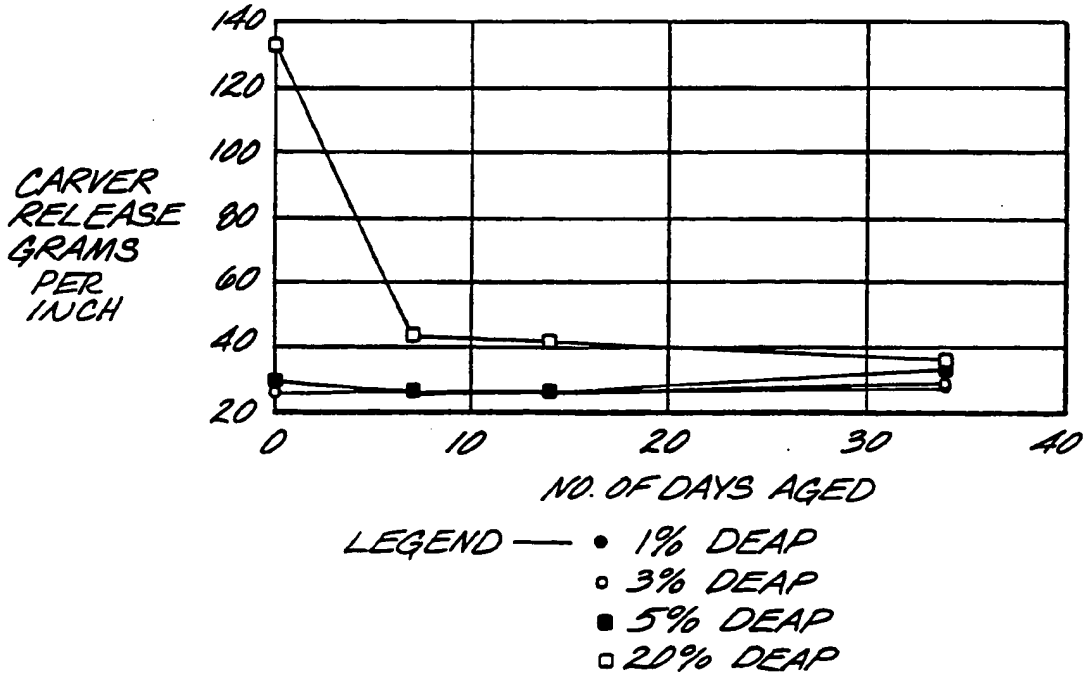
10
0 10 20 30 40 50 60 70 80 90 100
% 1530, BY WEIGHT
LEGEND — • 12ipm RELEASE
○ 1200 ipm RELEASE

Fig. 6


12 ipm / RT AGED
CARVER RELEASE GRAMS PER INCH
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120
100
80
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○ 3% DEAP
■ 5% DEAP
□ 20% DEAP

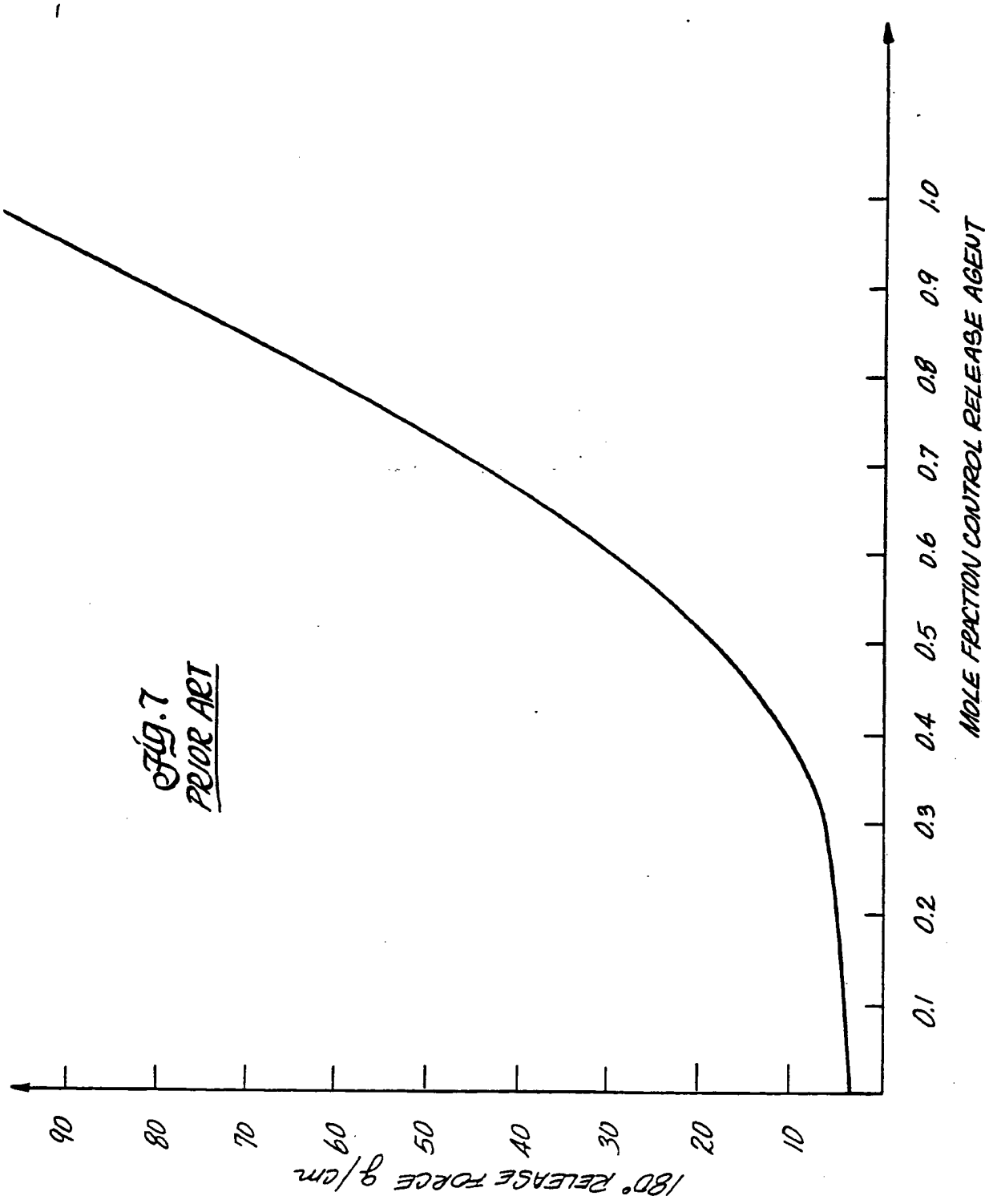

Fig. 7
PRIOR ART

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/01160

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. 4: B32B 9/04

US. CL. 428/40, 345, 352, 447; 525/474

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	428/40, 345, 352, 447 525/100, 474, 476, 479; 528/26

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4,288,479 (BRACK) 08 SEPTEMBER 1981	1-50
A,E	US, A, 4,668,558 (BARBER) 26 MAY 1987	1-50

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [1]

24 JUNE 1988

Date of Mailing of this International Search Report

02 AUG 1988

International Searching Authority

ISA/US

Signature of Authorized Officer

W. J. VANBALEN

Form PCT/ISA/210 (second sheet) (Rev.11-87)